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ORDERED LANGMUIR-BLODGETT FILMS OF POLYPYRROLE AND ANALOGS

AUTHOR'S
NAME

A.K.M. RAHMAN, L. SAMUELSON, D. MINEHAN, S. CLOUGH and S. TRIPATHY*

Polymer Science Program, University of Lowell, Lowell, MA 01854 (U.S.A.)

AUTHOR'S
AFFILIATION

T. INAGAKI, X.Q. YANG and T.A. SKOTHEIM

Brookhaven National Laboratories, Upton, NY 11973 (U.S.A.)

Y. OKAMOTO

Polytechnic University, Brooklyn, NY 11201 (U.S.A.)

ABSTRACT

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Ordered mono and multilayers of polypyrrole and its analogs were prepared using a Langmuir-Blodgett film balance. Films could be transferred with facility and were picked up on microscope grids for electron microscopic studies among a number of other investigations. Scanning electron microscopy (SEM) revealed a smooth coverage over a large surface area of the substrate. Electron diffraction from these thin films revealed that the nature of packing is substantially different from bulk grown polypyrrole.

INTRODUCTION

Over the past decade a number of conducting polymer systems have been developed that possess reasonable stability, in addition to being processible. The third order nonlinear optical susceptibility has been reported for some of these systems to be fairly large [1]. It will be desirable to process these materials into well ordered organization with controlled molecular architecture to fully utilize their unique electroactive properties. In addition, in better ordered systems the molecular basis for these properties may be established without ambiguity and improved facility.

In our laboratory, we have been investigating the electroactive properties of organized molecular assemblies in architectures which are appropriate for the desired measurement and compatible with integrated optics and electronics technologies. Using the Langmuir-Blodgett technique for example, monolayers of electrically conductive polymers may be prepared by simply spreading a soluble conducting polymer at the air-water interface. Alternatively, electrically conducting polymers may be prepared by spreading a mixed monolayer of pyrrole with a surface active derivative of pyrrole such as 3-hexadecylpyrrole on a L-B trough with a water subphase containing an oxidizing agent such as ferric chloride.

As the film is compressed, polymerization and doping take place at the interface resulting in a conducting polymer film. These films may then be subsequently transferred to the appropriate substrates. Unfortunately, in either case one does not have a classical monolayer in the sense that the growth is not dictated purely by hydrophilic-hydrophobic interaction of the surfactive molecules. Substantial possibility of multilayer stacking and uncontrolled growth in the interfacial polymerization at the interface exists.

* Author to whom correspondence should be sent.

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Microscopic studies in the present work, however, reveal monolithic layers that provide excellent coverage and support diffraction. These monolayers can then form ultrathin electrodes and interconnects, among other possibilities in multilayer superlattices where other optically active components are incorporated. For example, large local fields can be created across a bilayer between the conducting monolayers discussed earlier while maintaining a rather small potential difference.

In the present paper we describe the formation and morphological characteristics of L-B thin films created from a solution of polypyrrole and compare these to films prepared from the interfacial polymerization of pyrrole:3-hexadecylpyrrole mixed monolayer system.

EXPERIMENTAL

Monolayers of polypyrrole were prepared at the air-water interface from a mixed solvent system whose major component was tetrachloroethane using a commercial Lauda film balance. In addition, mixed monolayers of 3-hexadecylpyrrole to pyrrole in the ratio of 1 to 500 were spread onto the subphase which contained an oxidizing solution of 0.01M FeCl_3 . Details of the monolayer processing aspects will be submitted in a later communication. For scanning electron microscopy, films were transferred onto a clean glass substrate. For transmission electron microscopy and diffraction, on the other hand, films were transferred directly onto 200 and 1000 mesh electron microscope grids by both vertical and horizontal dipping techniques. The films were transferred to bare as well as carbon coated grids. The films were expected to be sufficiently conductive, such that further decoration to avoid charging in the microscope was not necessary.

For the purpose of comparison, thin films of polypyrrole were directly synthesized onto the electron microscope grids. The grids were made into a working electrode in an electrochemical cell containing an acetonitrile solution composed of 0.1M pyrrole and 0.1M tetraethyl ammonium toluene sulphonate. A constant cell current for a few seconds led to formation of a thin coating over the grid, often spanning a large portion of the empty spaces.

RESULTS AND DISCUSSION

3-hexadecylpyrrole (3HDP) and 3-hexadecylthiophene (3HDT) were selected for candidate materials as polypyrrole and polythiophene analogs for deposition at the air-water interface for a subsequent attempt at their polymerization at the air-water interface. The pyrrole ring of the 3HDP is sufficiently hydrophilic, due to the presence of the N-H bond such that the deposition characteristics of 3HDP are those of a classic surfactive molecule. Figure 1 shows the pressure-area isotherm of 3HDP at 20°C on a pure water subphase. The sharp slope and relatively small area per molecule at maximum surface pressure, 22 Å², suggests the molecules pack optimally in a vertical orientation as is typical of an ideal Langmuir-Blodgett system. The monolayer films at the air-water interface are also extremely stable as they may be annealed at constant pressure for long periods of time for subsequent deposition onto various substrates. Transfer of the 3HDP monolayers was performed with facility onto appropriate substrates to form multilayers with good transfer ratios. On the other hand, 3HDT does not form a monolayer film at the air-water interface and instead results in aggregated clusters. This may be due to the lack of hydrophilicity of the thiophene head group necessary to permit the monolayer formation.

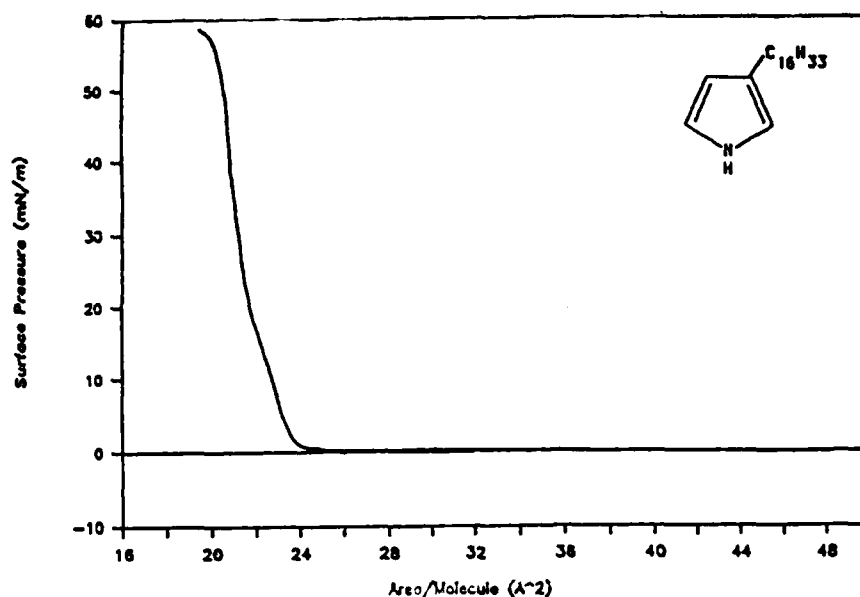
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Fig. 1. Pressure-area isotherm of 3HDP on a water subphase.

ABSTRACT

Transmission and grazing angle incidence spectra from mono and multilayers of 3HDP were carried out and the results have been reported elsewhere [2]. It was found that while a single monolayer transferred onto a platinum coated substrate may be sufficiently disordered, subsequent deposition of monolayers results in an ordered multilayer structure. Similar behavior for polydiacetylene mono and multilayers was observed by Chen et al. using surface enhanced Raman spectroscopic techniques [3].

Introduction of FeCl_3 into the subphase as a 3HDP monolayer is built up does not lead to polymerization to a sufficient extent through the pyrrole group. Upon exposure to the FeCl_3 subphase the 3HDP film shows an area expansion (Fig. 2) which is directly related to the concentration of FeCl_3 in the subphase. At high concentrations of FeCl_3 (0.1M for example), premature buckling of the film is observed as indicated by dark colored ripples of material on the subphase surface. There also appears to be a direct relationship between color of the collapsed films and concentration of the subphase, with the weaker concentrations, (0.001M), resulting in an orange colored material and the higher concentrations, (0.1M), resulting in a dark brown colored material.

The lowest energy conformation of the polypyrrole chain appears to be a planar extended chain where the adjacent pyrrole rings point in the opposite directions to each other [4]. If all the pyrrole rings were to point in the same direction a helical structure would be generated. In the 3HDP monolayer the pyrrole rings are all expected to point in the same direction (Fig 3A) and it is possible to argue on kinetic grounds why polymerization through the pyrrole ring in such a monolayer structure may not occur. If pyrrole molecules could be inserted between adjacent 3HDP molecules so as to permit (Fig 3B) alternate pyrrole groups to point in opposite directions, kinetic restriction may be alleviated. Unfortunately, pyrrole is extensively soluble in water and a 1:1 ratio of pyrrole to 3HDP when deposited at the air-water interface does not ensure this preferred arrangement either. A much higher ratio, 500:1, of pyrrole to 3HDP spread on the subphase containing 0.1M FeCl_3 however leads to extensive polymerization and a conductive film is obtained [5]. Alternatively, electrochemical polymerization in mixed multilayers of n-octadecane with surfactive pyrrole derivatives has been carried out by Shimidzu et al. [6]. It is possible, that the pyrrole groups from adjacent monolayers of a Y-type bilayer in this case provide the requisite configuration for an adequate polymerization condition.



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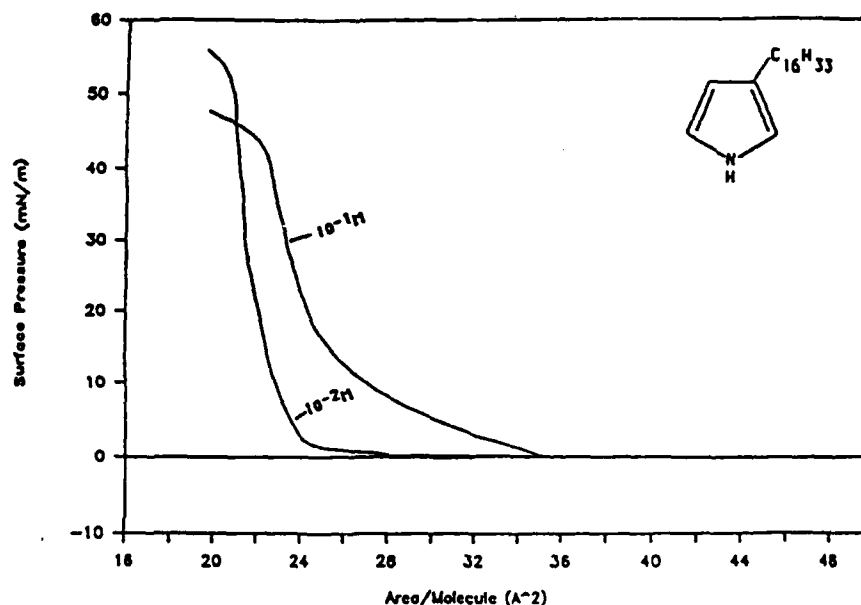


Fig. 2. Pressure-area isotherm of 3HDP on FeCl_3 subphase.

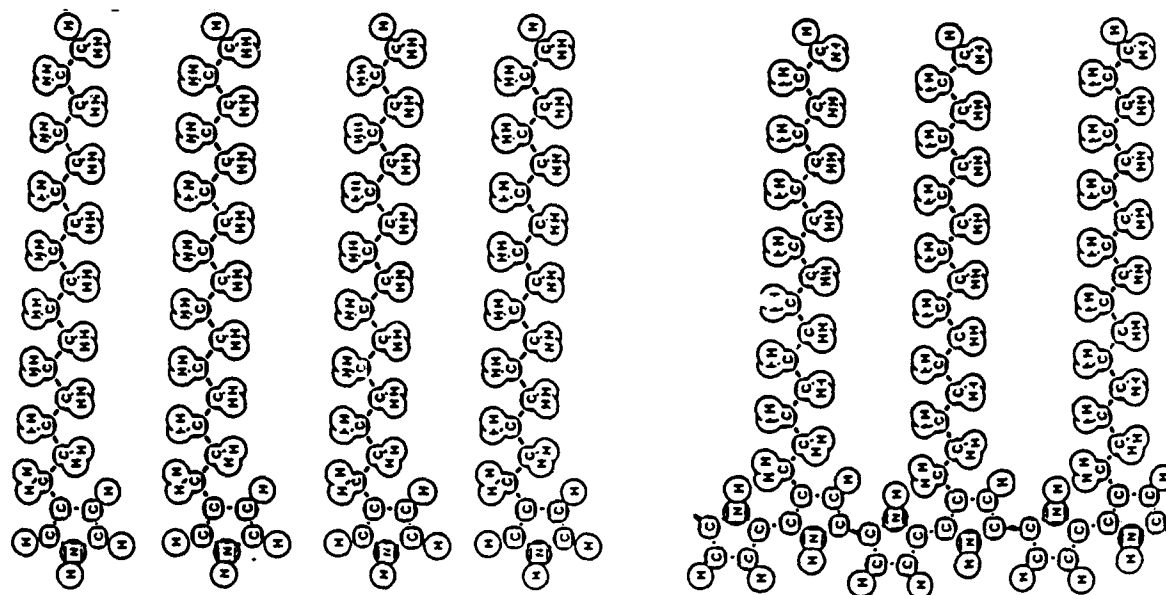


Fig. 3. A. Schematic of a 3HDP monolayer. B. Schematic of an alternative 3HDP:pyrrole monolayer.

The polymerized films were transferred onto electron microscope grids and imaged before and after washing with HCl to remove all FeCl_3 . Electron micrographs from monolayers of 500:1, pyrrole to 3HDP, before washing with HCl indicate the possibility of inclusion of excess FeCl_3 from the subphase. A relatively thick texture also indicates the possibility of polymerization of the excess pyrrole in the subphase once polymerization is initiated at the air-water interface. We propose that pyrrole monomers

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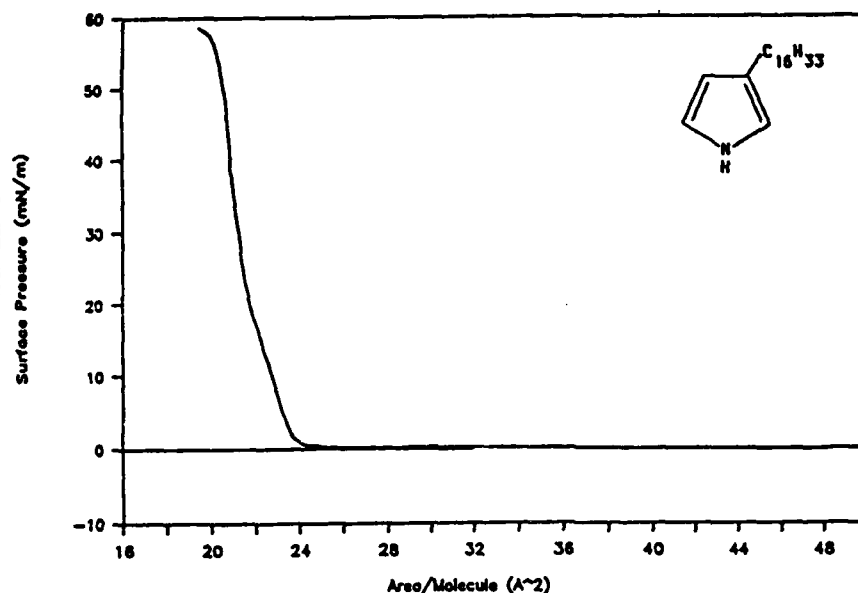


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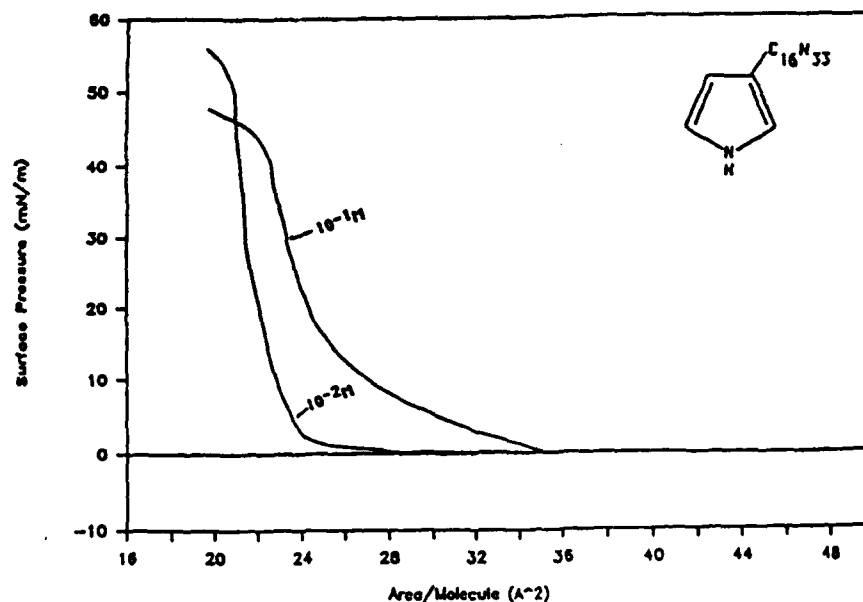


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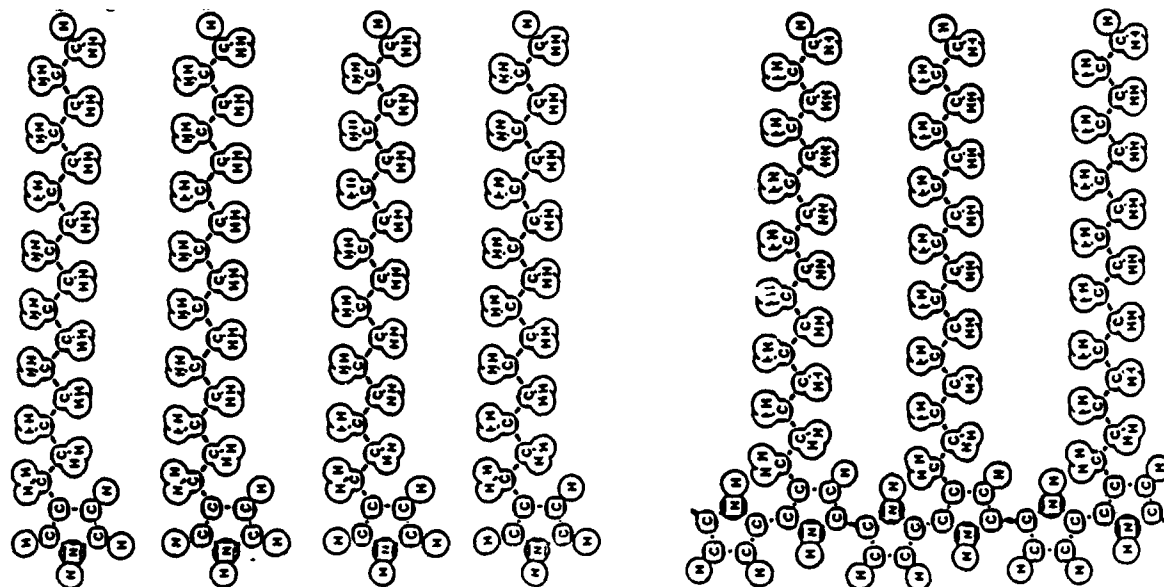


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may order themselves at the air-water interface onto the template of a 1:1 3HDP to pyrrole layer. Washing of the films with HCl tends to remove the excess FeCl_3 . Electron diffraction from the monolayer before and after washing confirms that the diffraction is from the polymer and not from FeCl_3 inclusions. This was further confirmed by allowing a FeCl_3 aqueous solution to evaporate on a carbon coated grid and subsequent diffraction which showed completely different diffraction patterns.

The diffraction pattern and corresponding "d" spacings from 500:1 pyrrole to 3HDP are shown in figure 4. The "d" spacings do not conform to the hexagonal packing of the alkyl side chains nor do they agree with those reported by Geiss [7] et al. and Buckley et al. [8] for electrochemically polymerized polypyrrole. This well defined diffraction pattern is also not observed from a monolayer of 3HDP.



$d_1=2.58\text{\AA}$
 $d_2=1.55\text{\AA}$
 $d_3=1.33\text{\AA}$
 $d_4=1.01\text{\AA}$
 $d_5=0.90\text{\AA}$

Fig. 4. Electron diffraction pattern from 500:1 pyrrole to 3HDP.

We conclude that the diffraction pattern is from the polypyrrole produced at the air-water interface formed in a new crystalline organization as growth and polymerization is initiated from a 1:1 3HDP to pyrrole two dimensional array as shown in figure 3B. Detailed crystal packing analysis and possible structure determination will be reported elsewhere.

The conclusion regarding the packing of polypyrrole chains growing from a two dimensional template is further supported by the diffraction results from monolayers of polypyrrole spread at the air-water interface directly from a polypyrrole solution in a mixed solvent system. Figure 5 is a transmission electron micrograph and figure 6 an electron diffraction pattern from monolayers of polypyrrole deposited at the air-water interface. The diffraction pattern is rather faint but the two lines that are clearly identified have the same "d" spacing as the diffraction pattern from the 3HDP:pyrrole system. Clearly, this monolayer has no possibility of inclusion of FeCl_3 and a two dimensional network of polypyrrole chains is expected.

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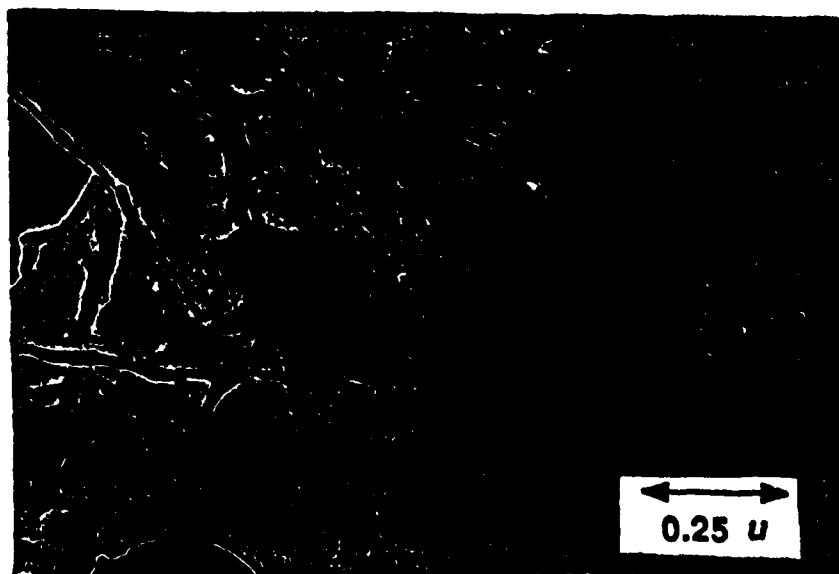


Fig. 5. TEM micrograph of polypyrrole monolayer on a bare copper grid.



$$d_1 = 2.54 \text{ \AA}$$

$$d_2 = 1.55 \text{ \AA}$$

Fig. 6. Electron diffraction pattern from a polypyrrole monolayer deposited from solution.

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ABSTRACT

The electron micrograph suggests a relatively smooth texture with some "buckling" up which is possibly an artifact of the film transfer process. The contrast between empty regions of the grid and from the film itself at this high magnification indicates the film to be very thin. However, it is not confirmed that the film is "monomolecular". The macromolecules lacking the standard structure of a surfactive molecule, containing a hydrophilic "head" and hydrophobic "tail" are not expected to form a well defined monolayer with constant thickness of the lateral dimension of this macromolecule. Further work is needed to ascertain the monomolecular nature of the layers.

The "folding over", tear and "buckling" that one sees in the transmission electron micrographs of these thin films are all possible artifacts of the transfer process onto a bare grid. The films were transferred onto a bare glass substrate and imaged in a scanning electron microscope. The SEM micrograph as shown in figure 7 clearly indicates smooth coverage as very large areas were scanned and the surface texture remains the same. Note that a bare glass substrate will show extensive charging in an electron beam and the polymer thin film was not decorated subsequent to transfer onto the glass substrate. A tear in the polymer film is clearly seen across the micrograph, as the bare glass surface shows up brighter than the area covered with the film. This tear was followed to about a millimeter distance upon which it terminated. The lack of charging of the polymer film indicates its conductive nature.

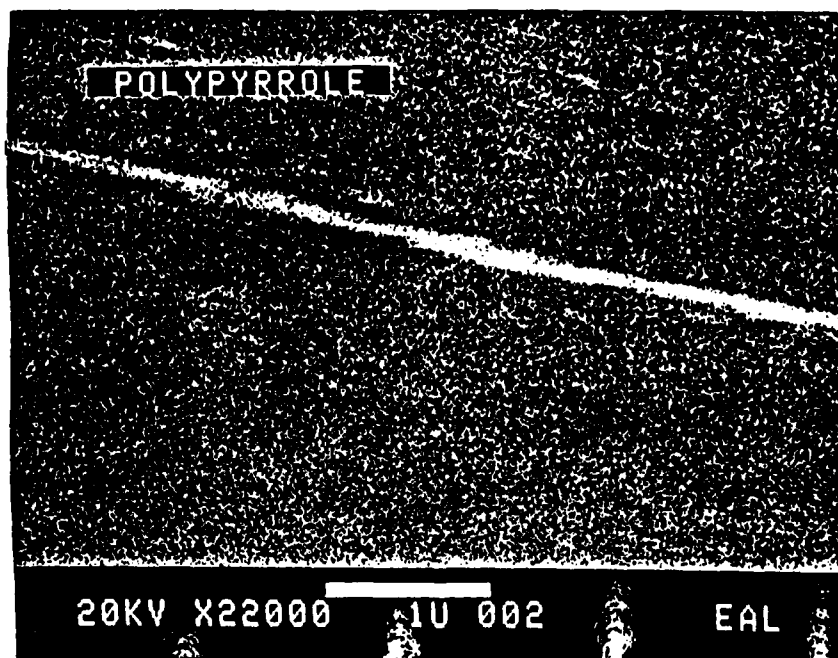


Fig. 7. SEM micrograph of a polypyrrole monolayer transferred onto a bare glass slide.

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CONCLUSION

The polypyrrole and its analogs have been grown in the form of large area thin films in a structural organization substantially different from bulk polymerized films. This organization is a direct result of confinement and controlled reaction in a two dimensional template at the air-water interface. The anticipated electroactive properties of these films in conjunction with their anisotropy and complex architecture in multilayer lattices are expected to yield rich dividends. These properties are presently being investigated and relevant structural information is reported in related papers of this conference.

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